UNIVERSITI PUTRA MALAYSIA

MULTIVARIATE OPTIMIZATION OF BIOSYNTHESIS OF TRIETHANOLAMINE-BASED ESTERQUAT CATIONIC SURFACTANT USING STATISTICAL ALGORITHMS

HAMID REZA FARD MASOUMI

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By

HAMID REZA FARD MASOUMI

Thesis Submitted to the School of Graduated Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for Degree of Doctor of Philosophy

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DEDICATION

This thesis is dedicated to my parents who have supported me all the way since the beginning of my studies.

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of requirement for the degree of Doctor of Philosophy

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Triethanolamine (TEA)-based esterquats are potential high-value products used as surfactants and softening agents. Chemical synthesis is the typical means to esterify triethanolamine and fatty acids. However, the reaction rate of triethanolamine- fatty acid esterification is usually low under high temperature. In this work, triethanolamine and oleic acid were chosen as substrates to design an optimal model reaction which will lead to high conversion rate utilizing lipase from *Candida antacrctica* (Novozyme 435) as biocatalyst in the organic solvent system. The investigated reaction conditions included enzyme amount, reaction time, reaction temperature, molar ratio of substrates and agitation speed. The major aim of this study was to model the effect of process parameters on the reaction yield. The most important stages in a process were modeling and optimization to improve a system and increase the efficiency of the process without increasing the cost. All process parameters are selected to conduct the optimization by

using some statistical algorithms such as Artificial Neural networks (ANNs), Response Surface Methodology (RSM), Wavelet Neural Network (WNN) and Partial Least Squares (PLS). In this regard, the related parameters of developed model were determined by applying chemometrics techniques on the experimental data. The optimized conditions was validated and applied to the synthesis of product. The next objective of the current study was to compare the performance of aforementioned algorithms with regard to predicting ability.

The investigation of TEA-based esterquat cationic surfactant synthesis was started in a 50 ml scale. The optimum condition derived from Taguchi experimental design were: enzyme loading 5.50 wt% of oleic acid, amount of oleic acid 17.70 mmol, amount of triethanolamine 8.85 mmol (molar ratio of substrates 1:2), reaction time of 14.44 hours and reaction temperature of 61°C. Comparison of predicted and actual values (48.42 and 49.94, respectively) revealed good correspondence between them, implying that empirical model derived from Taguchi experimental design can be used to adequately describe the relationship between the factors and response in Novozyme-catalyzed synthesis of TEA-based esterquat cationic surfactant at 50 ml scale. The relative deviation was obtained at 3.14% derived from Taguchi experimental design at 50 ml scale.

The optimum reaction condition derived from Taguchi experimental design was then employed in the 2000 ml scale. The effects of five independent variables (enzyme amount, reaction time, reaction temperature, molar ration of substrates and agitation

speed) were investigated, along with the mean predicted values for enzymatic reaction product. For this purpose, the response surface methodology (RSM), ANN-Quick Propagation (ANN-QP) and wavelet Neural network (WNN), using a central composite design (CCD), were adopted for predicting conversion reaction in optimal condition. Experiment was then carried out under the recommended condition and resulting response was compared to the predicted values. The optimum reaction parameters were: enzyme amount of 4.77 wt%, reaction time of 24 h, reaction temperature of 61.9°C, substrates molar ratio (OA:TEA) of 1:1mol (708 mmol of OA and TEA) and agitation speed of 480 r.p.m. The corresponding predicted value of percentage conversion was 62.64% as compared to the actual experimental value of 63.57%.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk ijazah Doktor Falsafah

OPTIMASI MULTIVARIAT DARI BIOSINTESIS KATIONIK SURFAKTAN ESTERQUAT BERASASKAN TRIETANOLAMINA MENGGUNAKAN ALGORITMA STATISTIK

Oleh

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Esterquats berbasis trietanolamina (TEA) adalah produk berpotensi nilai tinggi yang digunakan sebagai surfaktan dan agen pelembut. Sintesis kimia merupakan cara khas untuk mengesterifikasi trietanolamina dan asid lemak. Namun, kadar reaksi pengesteran asid lemak trietanolamina biasanya rendah pada suhu tinggi. Dalam kerja tesis ini, trietanolamina dan asid oleik dipilih sebagai substrat untuk merancang model tindakbalas optimum untuk memberikan kadar penukaran yang tinggi dan seterusnya dengan menggunakan algoritma statistik dan enzaim lipase *Candida antacrctica* (novozyme 435) sebagai biopemangkin dalam sistem pelarut organik. Keadaan tindakbalas yang dikaji meliputi amaun enzim, masa tindakbalas, suhu tindakbalas, nisbah molar substrat dan kelajuan pengacauan. Tujuan utama bagi pengkajian ini adalah untuk memodelisasikan kesan parameter proses terhadap hasil tindakbalas. Tahapan terpenting dalam proses ini adalah pemodelan dan pengoptimuman unuk menaiktarafkan sistem serta meningkatkan

kecekapan proses tanpa peningkatan kos. Semua parameter proses yang dipilih ini untuk melakukan pengoptimuman dengan menggunakan beberapa algoritma statistik seperti Rangkaian Saraf Tiruan (ANN), Kaedah Permukaan Rangsangan (RSM), Rangkaian Saraf Wavelet (WNN) dan Kuasa Dua Terkecil Separa (PLS). Dalam hal ini, parameter berkaitan untuk model yang dibangunkan telah ditentukan dengan mengaplikasikan teknik kemometrik pada data eksperimen. Keadaan optimum itu disahkan dan digunakan pada produk sintesis. Objektif kajian selanjutnya adalah membandingkan pencapaian algoritma tersebut dengan kemampuan untuk peramalan.

Kajian sintesis berasaskan TEA surfaktan kationik esterquat telah dimulakan dalam skala 50 ml. Keadaan optimum dari rekaan eksperimen Taguchi adalah: muatan enzim 5.50% berat asid oleik, amaun 17.70 mmol asid oleik, amaun trietanolamina 8.85 mmol (nisbah molar substrat 1:2), masa tindakbalas 14.44 jam dan suhu tidakbalas 61 °C. Perbandingan nilai ramalan dengan nilai sebenar (48.42 dan 49.94, masing-masing) mendedahkan korelasi yang baik antara mereka, membayangkan bahawa model empirik dari rekaan eksperimen Taguchi boleh digunakan dan sesuai untuk menggambarkan hubungan antara faktor dan tindakbalas dalam sintesis novozyme-mangkin TEA berasaskan esterquat kationik surfaktan pada skala 50 ml. Sisihan relatif diperolehi 3.14% bentuk rekaan eksperimen Taguchi pada skala 50 ml.

Keadaan tindakbalas optimum rekaan eksperimen Taguchi kemudian digunakan pada skala 2000 ml. Kesan dari lima pembolehubah bebas (amaun enzim, masa tindakbalas, suhu tindakbalas, nisbah molar substrat dan kelajuan pengacauan) diselidiki, bersama-

sama dengan nilai ramalan min untuk produk tindakbalas enzimatik. Untuk tujuan ini, Kaedah Permukaan Rangsangan (RSM), ANN-Cepat Perambatan (ANN-QP) dan Rangkaian Saraf Wavelet (WNN), dengan menggunakan rancangan komposit pusat (CCD), yang ditubuhkan untuk meramalkan tindakbalas penukaran pada keadaan optimum. Percubaan kemudian dilakukan di bawah keadaan yang disarankan dan tindakbalas yang dihasil dibandingkan dengan nilai ramalan. Parameter tindakbalas optimum adalah: amaun enzim 4.77% wt, masa tindakbalas 24 jam, suhu tindakbalas 61.9°C, nisbah molar substrat (OA: TEH) 1:1 mol (708 mmol OA dan TEA) dan kelajuan pengacauan 480 rpm. Nilai ramalan peratusan penukaran yang sesuai adalah 62.64% berbanding dengan nilai eksperimental sebenar 63.57%.

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In The Name of ALLAH, The Most Merciful and Most Beneficent

All praises do to Allah, Lord of the universe. Only by His grace and mercy this thesis can be completed.

I wish to express my foremost appreciation to Professor Dr. Anuar Kassim and Professor Dr. Mahiran Basri for patiently guiding me through the course of this thesis to its eventual end, enlightening me scientifically and resolving my technical crises. They were always there to provide everything I needed in the laboratory.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work expect for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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HAMID REZA FARD MASOUMI

DATE: 23 march 2011

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